Figure 3. Molar excess isobaric heat capacity, $C_p{}^E{}_m$, of aqueous 1-propanol mixtures vs. mole fraction, x, of water. Present work: (O) 288.15 K; (△) 308.15 K. Curves: (—) least-squares representations by eq 2; (···) smoothed results for 298.15 K (2).

Acknowledgment

We are indebted to Dr. O. Kiyohara for discussions of this work and to Mr. C. J. Halpin for technical assistance.

Glossary

$a_1, a_2,$ ···, a_j coefficients in representation of $C_p{}^E{}_m$ by eq 2

$C_{p,m}$	molar isobaric heat capacity, J K^{-1} mol^{-1}
V_m	molar volume, cm^3 mol^{-1}
x	mole fraction of water

Greek Letters

ϕ	volume fraction of water
ν	number of coefficients in eq 2
σ	standard deviation

Subscripts

1	water component
2	n-alcohol component

Superscripts

E	excess quantity
•	pure-component value

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Solubility of Oxalic Acid Dihydrate in Nitric and Sulfuric Acid Solutions at 0, 25, and 50 °C

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The solubility of oxalic acid dihydrate (ethanedioic acid) has been determined at 0, 25, and 50 °C in nitric–sulfuric acid solutions. This study covers four levels of nitric acid concentration in two concentrations of sulfuric acid. A mathematical model equation (log $S = A/T + B$, where S is oxalic acid solubility (wt %), T is the absolute temperature, and A and B are functions of the acid concentrations) was developed to predict the solubility of oxalic acid within the experimental ranges of the acid concentrations.

Introduction

One method for the production of oxalic acid is the use of nitric acid to oxidize cellulose in the presence of sulfuric acid

(1, 2). Values for the solubility of oxalic acid dihydrate in nitric–sulfuric acid solutions typical of those employed are required for the development of the process. Various authors (3–6) report the solubility of oxalic acid in single-mineral acids, but none give data for mixtures of these acids. The results reported here were obtained at three temperatures and four nitric acid concentrations in two levels of sulfuric acid concentration.

Experimental Section

Reagent-grade nitric acid, sulfuric acid, and oxalic acid dihydrate were used without further purification. Eight solutions of 100 g each were prepared of the initial compositions shown in Table I. $H_2C_2O_4 \cdot 2H_2O$ (21 g) was added to each of these solutions. The solutions were placed in a water bath at 25 ±

Table I. Solubility of Oxalic Acid Dihydrate in the System HNO_3-H_2SO_4-H_2O at 0, 25, and 50 °C

	soln no.	initial composition, wt %							
		1	2	3	4	5	6	7	8
HNO_3		4.94	9.91	14.90	19.80	4.79	10.02	14.95	19.35
H_2SO_4		39.79	40.00	39.90	39.80	48.30	49.70	49.79	49.45
H_2O		55.27	50.09	45.20	40.40	46.91	40.28	35.26	31.20

temp, °C	solubility of $C_2H_2O_4 \cdot 2H_2O$,[a] wt %															
	soln 1		soln 2		soln 3		soln 4		soln 5		soln 6		soln 7		soln 8	
	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
0	1.01	0.97	1.11	1.07	1.30	1.27	1.65	1.62	1.30	1.27	1.85	1.81	2.90	2.92	4.96	4.94
25	3.22	3.52	3.67	3.87	4.20	4.46	5.25	5.41	4.02	4.23	5.54	5.78	7.83	7.70	9.74	9.82
50	10.92	10.45	11.93	11.42	13.12	12.86	15.34	15.00	12.11	11.70	15.51	15.40	17.64	17.47	17.56	17.59

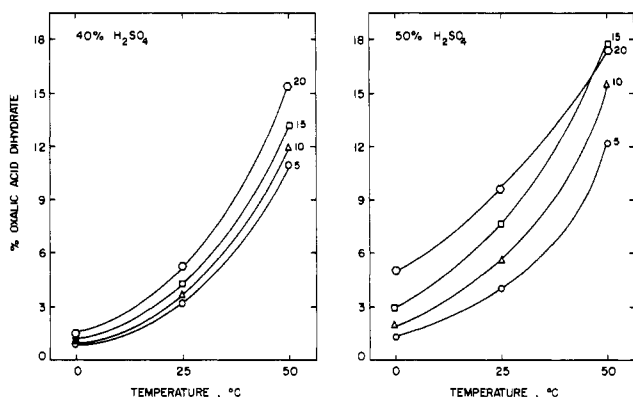[a] obsd = observed value; calcd = calculated value from the model eq 1.

Figure 1. Solubility of oxalic acid dihydrate in the temperature range 0–50 °C at four levels of HNO_3 in two levels of H_2SO_4 (numbers on curves denote initial % HNO_3).

Figure 2. Solubility of oxalic acid dihydrate in nitric–sulfuric acid mixtures.

0.1 °C and agitated at 4 rpm for a period of 7 days to establish the equilibrium conditions. They then were sampled for composition. These eight solutions then were placed in a cold room at 0 ± 0.5 °C and shaken periodically for 7 days before again being sampled for composition. The solutions then were placed in a water bath at 50 ± 0.1 °C and shaken periodically before sampling after 25 h. The short period of equilibration at 50 °C was chosen because slight oxidation of oxalic acid occurs at this elevated temperature (7). However, solid $H_2C_2O_4 \cdot 2H_2O$ was present in the solutions at all times.

The oxalic acid dihydrate was determined by precipitation as calcium oxalate. Determination of nitric acid was by the Kjeldahl method. Sulfuric acid was determined by difference after titration with standard NaOH.

Results and Discussion

The results are given in Table I and shown in Figure 1. At the 40% sulfuric acid level there was an increase in the amount of oxalic acid dihydrate in solution as the nitric acid concentration increased (Figure 2). The same is true at the 50% sulfuric acid level, with the exception that at 50 °C the 20% nitric acid solution contained less oxalic acid dihydrate in solution than the 15% nitric acid solution.

Figure 1 shows that for 40% sulfuric acid the oxalic acid dihydrate in solution increases 1.6 times at 0 and 25 °C for a fourfold increase in nitric acid; at 50 °C the increase is 1.3. At the 50% sulfuric acid level this uniformity of increased solubility does not hold true.

Figure 2 shows the oxalic acid dihydrate solubility as a function of the ratio HNO_3/H_2SO_4. There is a flattening of the solubility curves at the higher ratios HNO_3/H_2SO_4 at 25 and 50 °C for the 50% sulfuric acid solution. This indicates that in the 50% sulfuric acid solutions the maximum solubility with increase in nitric acid concentration is being approached.
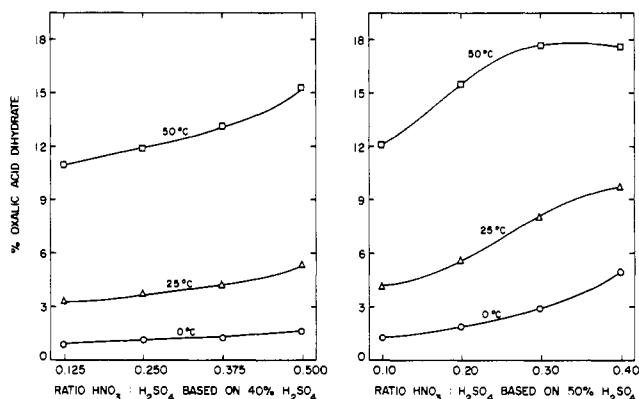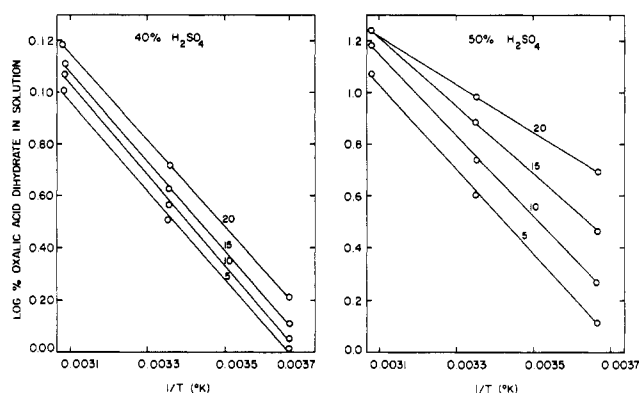

Figure 3. Solubility of oxalic acid dihydrate as related to reciprocal of absolute temperature (numbers on curves denote initial % HNO_3).

Solubility of the oxalic acid in the acid mixtures always increased when the solution temperature increased from 0 to 50 °C (Figures 1 and 2). This solubility–temperature relationship can be expressed as a straight line according to the following Arrhenius-type expression:
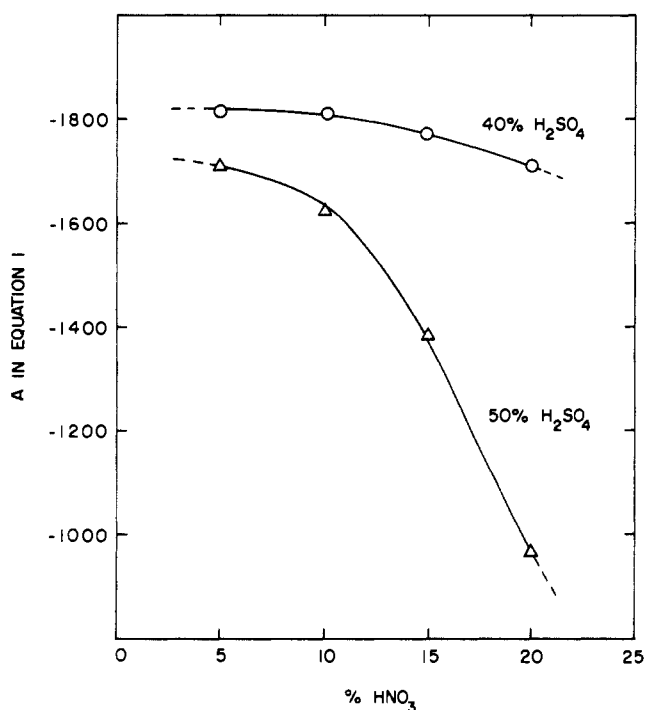
$$\log S = A/T + B \tag{1}$$

where S is the solubility of the oxalic acid in wt %, T is the absolute temperature, and A and B are constants for each test. As shown below, A and B are functions of the acid composition in the initial solution before the addition of oxalic acid. Figure 3 shows plots of $\log S$ vs. $1/T$ where A is the slope and B is the intercept of the lines. Each A and each B were evaluated by a regression analysis and are listed in Table II as the observed values. Average heat of dissolution, ΔH (kcal), is obtained from the slopes of the lines since

$$\Delta H = -2.303RA \tag{2}$$

Table II. Constants for Solubility of Oxalic Acid Dihydrate in the System HNO_3-H_2SO_4-H_2O ($\log S = A/T + B$)

soln no.	A obsd[a]	A calcd[b]	B obsd[a]	B calcd[c]	ΔH, kcal obsd[a]	ΔH, kcal calcd[d]
1	−1819.48	−1821.48	6.6480	6.6559	8.325	8.334
2	−1816.61	−1812.46	6.6837	6.6665	8.312	8.292
3	−1768.84	−1772.81	6.5787	6.5953	8.093	8.111
4	−1707.18	−1702.69	6.4606	6.4545	7.811	7.804
5	−1707.42	−1702.96	6.3540	6.3381	7.812	7.791
6	−1627.71	−1640.12	6.2187	6.2629	7.447	7.504
7	−1384.75	−1371.38	5.5338	5.4861	6.336	6.274
8	−968.74	−973.83	4.2406	4.2587	4.432	4.456
r^2		0.999		0.999		0.999
SD		14.45		0.0524		0.066
standard % error		0.90		0.86		0.90

[a] obsd = observed values obtained by regression. [b] calcd = calculated values from eq 3. [c] calcd = calculated values from eq 4. [d] calcd = calculated values from eq 5.

Table III. Constants for Calculating Slope (A), Intercept (B), and Heat of Solution (ΔH) of Oxalic Acid Dihydrate in Nitric-Sulfuric Acid Solutions

A	B	ΔH, kcal
$a_0 = -2941.9622128$	$b_0 = 10.4033362$	$d_0 = 13460.2602738$
$a_1 = 28.8448491$	$b_1 = -0.0967797$	$d_1 = -131.9728629$
$a_2 = 188.4367710$	$b_2 = -0.7182172$	$d_2 = -862.1483893$
$a_3 = -4.9585029$	$b_3 = 0.0187940$	$d_3 = 22.6864710$
$a_4 = -14.6061110$	$b_4 = 0.0509961$	$d_4 = 66.8268461$
$a_5 = 0.3839517$	$b_5 = -0.0013253$	$d_5 = -1.7566814$
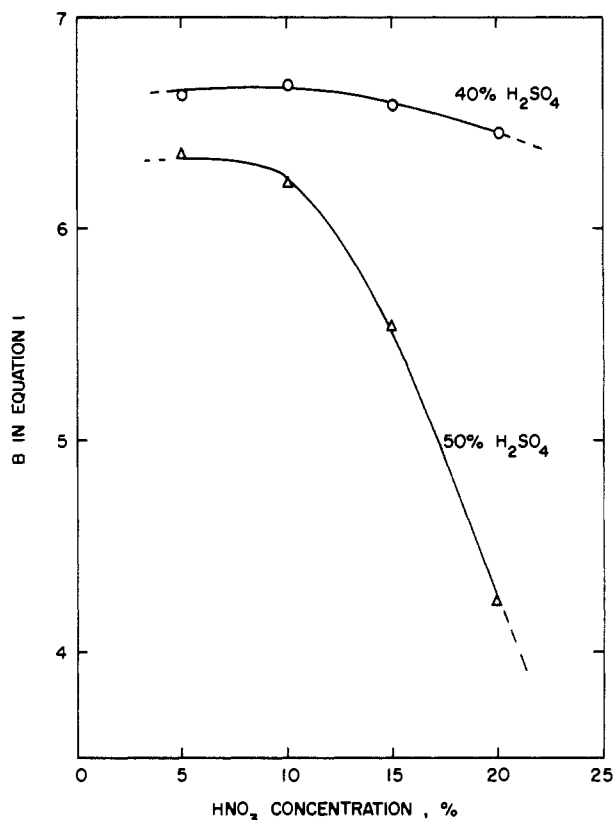
Figure 5. Relationship between B in eq 1 and the initial acid concentrations (solid lines are calculated from eq 4).

Figure 4. Relationship between A in eq 1 and the initial acid concentrations (solid lines are calculated from eq 3).

where R is the gas constant (listed in Table II as the observed values). Examination of the constants A, B, and ΔH showed that they are a function of the initial acid concentration. After a few trials to fit the data to model equations, the following equations were found to best represent the data:

$$A = a_0 + a_1 C_s + (a_2 + a_3 C_s)C_n + (a_4 + a_5 C_s)C_n^2 \quad (3)$$

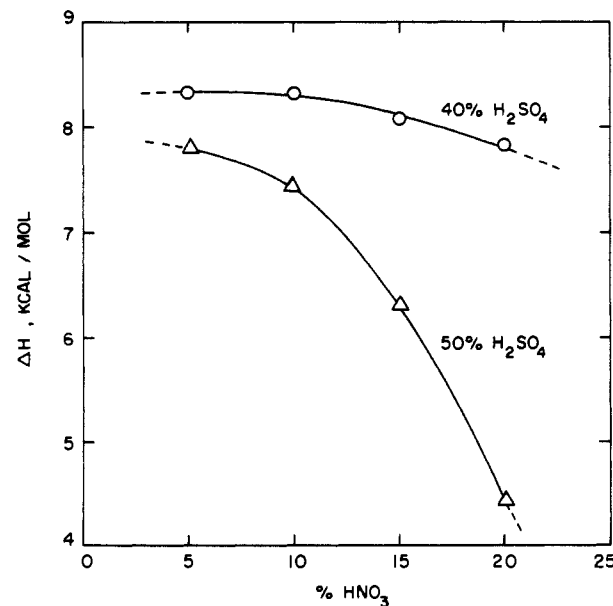$$B = b_0 + b_1 C_s + (b_2 + b_3 C_s)C_n + (b_4 + b_5 C_s)C_n^2 \quad (4)$$

$$\Delta H = d_0 + d_1 C_s + (d_2 + d_3 C_s)C_n + (d_4 + d_5 C_s)C_n^2 \quad (5)$$

where C_s and C_n are the initial weight percent concentrations of sulfuric and nitric acids, respectively, and a_i, b_i, and d_i are coefficients for each term. These coefficients are listed in Table III. Calculated values of A, B, and ΔH are evaluated for each test solution by using eq 3-5, respectively, and are listed in Table II as calculated values and are shown in Figures 4-6.

Agreement between observed and calculated values for all three constants is excellent. The correlation constant, r^2, is 0.999 for all cases. The standard percent error of the calculated values is less than 1% for A, B, and ΔH. These good

Figure 6. Relationship between heat of dissolution, ΔH, and the initial acid concentrations (solid lines are calculated from eq 5).

agreements are demonstrated in Figures 4–6, where the lines represent the calculated values from eq 4–6, respectively.

With these developed parameters the solubility of oxalic acid dihydrate was calculated for the test solutions and listed as the calculated values in Table I. There is good agreement between calculated and observed values. Therefore, eq 1 can be used as a model to predict the solubility of the oxalic acid in mixtures of nitric and sulfuric acids when the concentration of these mineral acids is known.

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Activity Coefficients at Infinite Dilution by Gas–Liquid Chromatography. 1. Hydrocarbons and *n*-Chloroparaffins in Organic Solvents

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Activity coefficients at infinite dilution of paraffins, olefins, aromatics, and *n*-chloroparaffins in 12 stationary phases were determined by gas chromatography. The stationary phases employed were *n*-hexadecane, *n*-octadecane, *n*-tetracosane, 1-hexadecene, 1-octadecene, 1-chlorohexadecane, 1-chlorooctadecane, 1-dodecanol, 1-tetradecanol, 10-nonadecanone, 2-dodecanone, and 9-heptadecanone. The investigation was carried out at temperatures ranging from 30 to 80 °C.

Introduction

Fluid-phase equilibrium data at low pressures are usually interpreted through excess functions. This means that it is possible to calculate the compositions of the phases at equilibrium from the excess quantities (activity coefficients) for the liquid mixtures and, vice versa, the excess quantities of the liquid phase from the experimentally determined compositions of the phases. In both cases, it is generally useful to have a model which expresses the variation of the excess quantity as a function of various variables (temperature, pressure, and composition), so that the effect of such quantities on equilibrium can be evaluated correctly.

In the building up of a thermodynamical model, the effect of pressure is usually neglected and that of temperature is considered a secondary one. In other words, the model is built up principally to provide the composition dependence of the excess quantity, primarily of excess free energy. The effect of the temperature is often added subsequently, by considering the temperature dependence of the parameters which are included in the model.

The majority of liquid-solution models contain two arbitrary parameters per binary pair. Generally, such parameters are not determinable a priori.

Even if we consider the limitations involved in the use of binary constants alone, the calculation of any equilibrium for a multicomponent system (n = number of components) will require the knowledge of $n(n - 1)$ interaction parameters. Even when we use methods which allow rapid and accurate experimental determinations, the amount of work required will obviously be enormous, even if we are "lucky" enough to have

Table I. Solute Components

solute no.	compd	solute no.	compd
1	*n*-pentane	10	methylcyclohexane
2	*n*-hexane	11	ethylcyclohexane
3	*n*-heptane	12	benzene
4	*n*-octane	13	toluene
5	1-pentene	14	ethylbenzene
6	1-hexene	15	1-chloropropane
7	1-heptene	16	1-chlorobutane
8	1-octene	17	1-chloropentane
9	cyclohexane	18	1-chlorohexane

Table II. Activity Coefficients at Infinite Dilution in *n*-Hexadecane

solutes	temp, °C	31.7	42.2	51.3
2		0.91	0.92	0.87
3		0.93	0.93	0.93
5			0.92	
6		0.95	0.93	0.92
7		0.96	0.96	0.94
12		1.04[a]	1.03[b]	
13		1.05[a]	1.04[b]	
16		1.18	1.16	1.12
17		1.19	1.17	1.13

[a] 38.9 °C. [b] 43.8 °C.

Table III. Activity Coefficients at Infinite Dilution in *n*-Octadecane

solutes	temp, °C	51.4	61.4	70.5	80.5
2		0.85	0.86	0.88	0.86
3		0.86	0.89	0.89	0.88
6		0.85		0.88	0.86
7		0.88	0.90	0.90	0.89
12		1.03	1.03[a]	1.03[b]	1.02[c]
13		1.03	1.04[a]	1.04[b]	1.04[c]
14			1.12[a]	1.13[b]	1.13[c]
16		1.02	1.03	1.05	0.99
17		1.02	1.05	1.03	1.02

[a] 60.0 °C. [b] 68.8 °C. [c] 78.8 °C.

at our disposal data for some binary mixtures. In view of these considerations, the methods based on group contribution come into use because they allow the infinite variety of organic compounds to be reduced to a large but finite number of or-